THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Toshihiko OHASHI et al.

Serial No.: 10/541,776

Filed : July 8, 2005

For : SILICA-CONTAINING LAMINATED STRUCTURE, AND COMPOSITION FOR USE IN FORMING A POROUS SILICA LAYER

Art Unit : 1771

Examiner : Victor S Chang

DECLARATION

I, Masayuki NAKATANI, a Japanese citizen residing at Suntopia Fuji 102, 126-1, Nakamaru, Fuji-shi, Shizuoka-ken, Japan, hereby declare and state:

I took a master course majoring in chemistry at Graduate School of Science, Hiroshima University, Japan, and I was graduated therefrom in March 1984.

I entered Asahi Kasei Kabushiki Kaisha in April 1984. I was engaged in the research and development of engineering materials from 1984 to 2004. Then, I have been engaged in the research and development of optical thin films to date.

I am well familiar with the present case.

I have read and understood the Office Action dated August 28, 2007 and the references cited therein.

I have made observations to determine the reflectance values of the "coated articles" produced in the Examples of U.S. Patent No. 4,816,333 (**Lange**) and the refractive indices of the porous silica coatings formed in the Examples of **Lange**, and observations on the difference in optical characteristics between the coated article of **Lange** and the coated article of the present invention. The method and results are as described in a paper attached hereto and marked "Exhibit 1".

From the results of Exhibit 1, it can be fairly concluded:

(1-1) that the reflectance of the coated article of **Lange** is **1.0 % at the lowest** (measured at a wavelength of 600 nm with respect to one surface of the sample), which is still **higher than** the reflectance (0.1 to 0.45 %) recited in claim 1 of the present application,

(1-2) that the calculated refractive index (with respect to one surface of the sample) is **1.382 at the lowest**, which is still **higher than** the refractive index (1.22 to 1.30) recited in claim 1 of the present application,

(1-3) that, with respect to the relationship between the porosity of the porous silica coating and the refractive index

(RI), which is represented by the formula shown at col. 4, line 45 of **Lange**, such a relationship is **nothing more than a generally theory**, and does **not** mean that **Lange** can provide a silica coating having an "index of refraction of from about 1.15 to 1.40, preferably 1.20 to 1.30" **without sacrificing** the strength of the silica coating,

(1-4) that the only optical characteristic that is actually measured in **Lange** is the transmittance from which the above-mentioned reflectance and refractive index are determined, and

(1-5) that, therefore, it is apparent that the optical characteristics (the refractive index and the minimum reflectance) as recited in claim 1 of the present application can**not** be achieved by **Lange** while maintaining the strength of the porous silica coating at a practically acceptable level (i.e., a pencil hardness of H or higher as measured in accordance with JIS K5400 under a load of 1 kg, using a testing pencil as defined in JIS S6006).

Further, in order to confirm the results of the observations made in Exhibit 1, I have conducted experiments to evaluate the reflectance of the "coated articles" produced in the Examples of U.S. Patent No. 4,816,333 (**Lange**), and the refractivity and strength of the silica coatings of the coated articles. The method and results are as described in

a paper attached hereto and marked "Exhibit 2".

From the results of Exhibit 2, it can be fairly concluded:

(2-1) that the reflectance of the coated article produced in accordance of **Lange** (at all wavelengths including those used in the present application for the measurement of minimum reflectance) is much **higher** than the range (0.1 to 0.45 %) recited in claim 1 of the present application,

(2-2) that the refractive index of the silica coating formed in accordance with **Lange** is **1.364 at the lowest**, which is still **higher** than the range (1.22 or more and less than 1.30) recited in claim 1 of the present application,

(2-3) that the silica coating formed in accordance with **Lange** has a pencil hardness **lower than "H"**,

(2-4) that the above-mentioned poor optical characteristics and poor strength in **Lange** (as compared to the present invention) are attributable to the difference in structure of the silica coatings,

(2-5) that, thus, it has been confirmed that, by the technique of **Lange**, it is impossible to obtain the silica-containing laminated structure of the present invention which is advantageous in that the porous silica layer has not only low refractivity but also high strength, and, thus, the results of Exhibit 1 have been confirmed.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

February 25, 2008
Date

Masayuki Nakatani
Masayuki NAKATANI

Exhibit 1

Observations to determine the reflectance values of the "coated articles" produced in the Examples of U.S. Patent No. 4,816,333 (**Lange**) and the refractive indices of the porous silica coatings formed in the Examples of **Lange**, and observations on the difference in optical characteristics between the coated article of **Lange** and the coated article of the present invention

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1. Object of the observations:

U.S. Patent No. 4,816,333 (**Lange**) attempts to improve the light transmission of a coated article having a porous silica coating (col. 2, lines 53 to 64 of **Lange**). In the Examples of **Lange**, both of transmission and reflectance are measured in Example 1 (col. 6, lines 46 to 58), and only transmission is measured in the rest of the Examples (Table 2 on cols. 7 and 8).

As pointed out by the Examiner, the refractive index of a porous coating is mentioned in **Lange**, but is mentioned only in connection with a **theoretical relationship** between the refractive index and the porosity. In nowhere in **Lange** is it shown that **Lange** can provide a porous silica coating having a refractive index as mentioned in **Lange** while maintaining the

strength of the porous silica coating at a practically acceptable level.

In order to evaluate the reflectance and the actual refractive index in **Lange**, the reflectance values and the refractive indices in the Examples of **Lange** are calculated below from the transmission values shown in the Examples of **Lange**.

2. Method:

(2-1) Calculation of reflectance

2-1a. Relationship between transmission and reflectance

It is well known in the art that transparent optical materials absorb no or substantially no visible light since the absorption of visible light by a material causes the material to assume a color. Therefore, transmission (%) + reflectance (%) = 100 %. This is also apparent from Example 1 of **Lange** (col. 6, lines 50 to 58) wherein:

the control (uncoated sample) has a reflectance of "about **12 %**" and a light transmission of "about **88 %**", and

the coated sample has a reflectance of "about **2 %**" and a light transmission of "about **98 %**".

That is, in both of the uncoated sample and the coated sample, transmission (%) + reflectance (%) = 100 %.

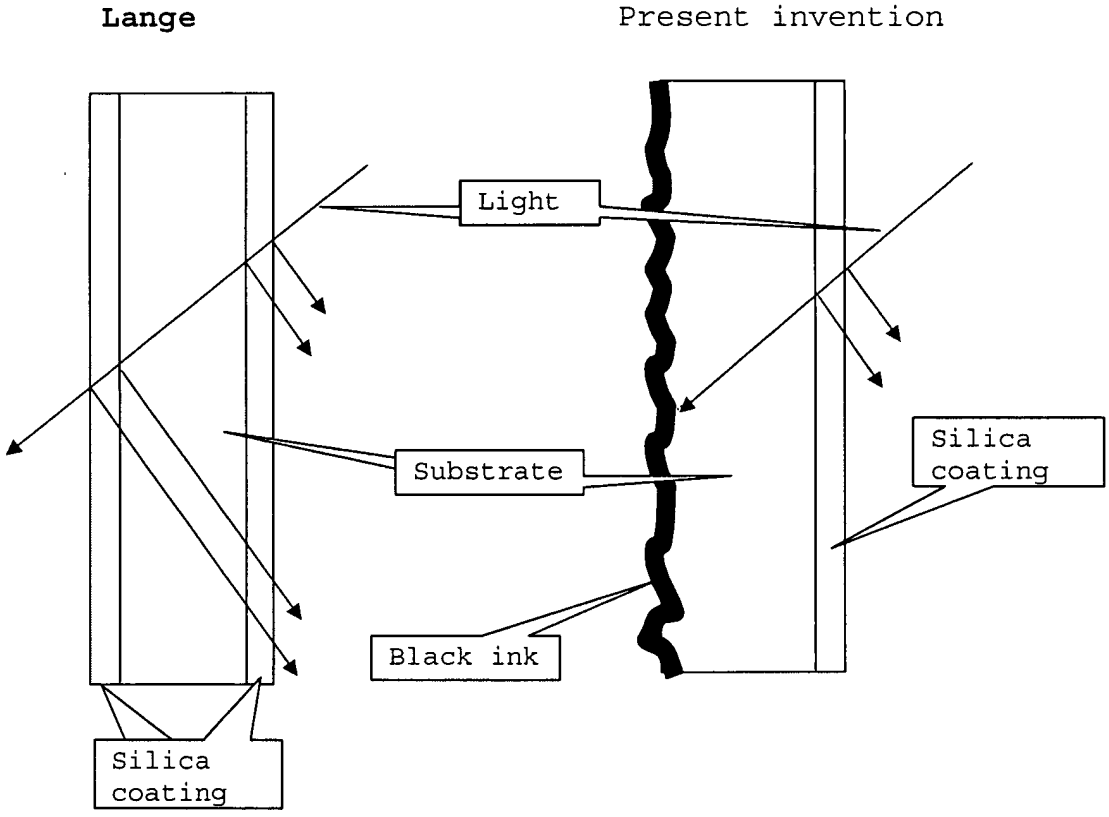
Accordingly, from the transmission values at 600 nm shown in Table 2 on cols. 7 and 8 of **Lange**, the respective reflectance values (%) are calculated by the formula: 100 (%) - transmission (%). From the various measurement wavelengths used in the Examples of **Lange**, 600 nm is chosen since 600 nm is the only wavelength mentioned in Example 1 of **Lange** and is close to those (550 to 570 nm) used in the measurements performed in the Examples of the present application (this is because the reflectance around 550 nm is particularly important for antireflection materials).

2-1b. Difference in samples used in the Examples of the present application and the Examples of **Lange**

In the Examples of **Lange**, the transmission (%) is measured with respect to samples each having porous silica coatings formed on **both surfaces** thereof by dipping or wiping (col.6, lines 24-27, and col.7, lines 36-41 of **Lange**). On the other hand, in the Examples of the present application, the reflectance is measured with respect to samples each having a silica coating formed on only **one surface** thereof (page 73, lines 1 to 10 of the specification of the present application). (Specifically, in the Examples of the present application, a silica coating is formed on only **one surface** of a

substrate, and the other surface is roughened and coated with **black ink** so as to prevent the reflection of light (which has entered into the substrate from the coated surface) at the uncoated surface of the substrate). This difference in the samples used in **Lange** and the present application is illustratively shown in Fig. A below.

Fig. A



Therefore, for fair comparison between the reflectance values in the Examples of **Lange** and the reflectance values in

the Examples of the present application, the reflectance values in the Examples of **Lange** are halved.

(2-2) Refractive indices of silica coatings formed in the Examples of **Lange**

From the reflectance values calculated in item 2-1b and the thicknesses of substrates described in **Lange**, the refractive indices of the substrates and silica coatings in the Examples of **Lange** are calculated by an add-in software for Microsoft Excel, which is contained in a CD-ROM attached to a book entitled "Simulation Technique and Optimal Design about Optical Multilayered Films by Excel VBA", published by Technical Information Institute Co., Ltd., Japan, on the assumption that there is no chromatic dispersion. This add-in software calculates refractive indices by the so-called "matrix method" (see, for example, Born M., Wolf E., 1980, Principles of optics, 6th ed. New York: Pergamon Pres). Using this add-in software, the refractive indices of the substrates used in the Examples of **Lange** are determined by imputing the respective reflectance values. Then, by imputing the obtained refractive indices of the substrates and the thicknesses of the substrates, the refractive indices of the porous silica coatings formed in the Examples of **Lange** are

determined.

(2-3) Results of the determinations of the reflectance values of the coated articles produced in the Examples of **Lange** and the refractive indices of the porous silica coatings formed in the Examples of **Lange**

The results of the calculations made in items (2-1) and (2-2) above are shown in Table A below, together with relevant data excerpted from Table 1 on cols. 7 and 8 of **Lange** and the descriptions in Examples of **Lange**.

Table A

Ex.	Material (substrate)	Coating	Transmission and reflectance (600 nm)			Refractive index calculated		
			Transmission (%) described	Reflectance (%) calculated (both surfaces)	Reflectance (%) calculated (one surface)	Substrate	Coating thickness:120 nm	Coating thickness: 100nm
1	Biaxially oriented PET film	*none (substrate only)*	*88.0*	*12*	*6.00*	*1.650*	-	-
	Ditto	dip	**98.0**	**2**	**1.00**	**-**	**1.405**	**-**
3 (*control*)	A(polymethyl enemethacrylate)	*none (substrate only)*	*92.5*	*7.5*	*3.75*	*1.480*	-	-
4	A	dip	**94.5**	**5.5**	**2.75**	**-**	**1.436**	**1.438**
5	A	wipe	**94.7**	**5.3**	**2.65**	**-**	**1.431**	**1.434**
6 (*control*)	B(polycarbonate, CR-39)	*none (substrate only)*	*91.0*	*9.0*	*4.50*	*1.539*	-	-
7	B	wipe	**97.5**	**2.5**	**1.25**	**-**	**1.382**	**1.385**
8	B	wipe	**96.0**	**4.0**	**2.00**	**-**	**1.424**	**1.430**
9	B	wipe	**97.4**	**2.6**	**1.30**	**-**	**1.385**	**1.388**
10	B	wipe	**97.0**	**3.0**	**1.50**	**-**	**1.397**	**1.401**
11 (*control*)	C(Lexan)	*none (substrate only)*	*92.0*	*8.0*	*4.00*	*1.500*	-	-
12	C	wipe	**94.1**	**5.9**	**2.95**	**-**	**1.454**	**1.457**
13 (*control*)	D(cellulose acetate butyrate)	*none (substrate only)*	*87.5*	*12.5*	*6.25*	*1.667*	-	-
14	D	dip	**93.7**	**6.3**	**3.15**	**-**	**1.526**	**1.544**
15	D	wipe	**89.1**	**10.9**	**5.45**	**-**	**1.630**	**1.637**

From Table A above, it is apparent that, even when the reflectance values in the Examples of **Lange** are halved for the reason mentioned in item 2-1b above, the reflectance values of the coated articles obtained in the Examples of **Lange** are still **larger** than the "minimum reflectance of from 0.1 to 0.45 %" recited in claim 1 of the present application. (For information, it should be noted that, among all of the transmission values shown in Table 2 of Lange measured at 400, 500, 600, 700 and 800, the highest transmission value is "98.2", which means that, in the Examples of **Lange**, the lowest reflectance measured on both surfaces of the sample is 1.8 % and the lowest reflectance measured on one surface of the sample is 0.9 %, which is still **larger** than the "minimum reflectance of from 0.1 to 0.45 %" recited in claim 1 of the present application.)

(2-4) Observations on the difference in optical characteristics between the coated article in accordance with **Lange** and the coated article according to the present invention

Since **Lange** attempts to improve the transmission of the coated article (see, for example, col. 2, lines 53 to 64 of **Lange**), it is reasonable to consider that the im-

provements in the reflectivity values and the refractive indices in the Examples of **Lange** are at the highest levels as far as the technique of **Lange** is put into practice.

As pointed out by the Examiner, **Lange** explains the relationship between the porosity of the porous silica coating and the refractive index (RI) of the porous silica coating. Specifically, **Lange** describes as follows:

> "These subwavelength interstices whivh are present throughout the coating later, provide a coating which may have a calculated index of refraction of from about 1.15 to 1.40, preferably 1.20 to 1.30 depending on the porosity of the coating. When the porosity of the coating is high, e.g., about 70 percent, lower values for the index of refraction are obtained. When the porosity of the coating is low, e.g., 25 percent, higher values for the index of refraction are obtained. The index of refraction of the coating is dependent on the relative volume ratios of the particles and the interstices and the index of the refraction of the silica, i.e., 1.47. For purposes of this invention, the index of refraction (RI) is calculated using the formula:
>
> $$RI = \frac{Po}{100} + \left(\frac{100 - Po}{100}\right)1.47$$
>
> where the Po is the value of the open porosity." (emphasis added) (col. 4, lines 28 to 46 of **Lange**)

As apparent from the above-quoted description and as

is also apparent for those having ordinary skill in the art, the RI-porosity relationship represented by the formula is **nothing more than a generally theory** on some assumptions, and does **not** mean that **Lange** can provide a porous silica coating having an "index of refraction of from about 1.15 to 1.40, preferably 1.20 to 1.30" **without sacrificing** the strength of the porous silica coating, which tends to be lowered when the porosity is increased to improve the refractive index. Specifically, the above formula means that, since the refractive index of silica is 1.47 and the refractive index of air is 1, the refractive index of a porous silica film can be directly derived from the porosity as in the above-mentioned formula described in **Lange**. However, actually, the RI is influenced by various factors, such as unevenness in thickness, impurities (e.g., a substance having a high RI dissolved out from the substrate) in the porous silica coating, etc. Further, in the above-mentioned formula, the **strength** needed of a silica film used as an antireflection film is **not** taken in to consideration.

In fact, as shown in Table A above, the reflectance of the coated article of **Lange** is 1.0 % at the lowest (measured at a wavelength of 600 nm with respect to one surface of the sample), which is higher than the reflec-

tance (0.1 to 0.45 %) recited in claim 1 of the present application. Further, the calculated refractive index (with respect to one surface of the sample) is 1.382 at the lowest, which is also higher than the refractive index (1.22 to 1.30) recited in claim 1 of the present application. As apparent for those skilled in the art, the reason for this is that, by the conventional technique using non-agglomerated silica particles, the porosity of a porous silica coating used as an antireflection film can**not** be increased so much while maintaining the strength of the silica coating at a practically acceptable level.

The reason for the above-mentioned difference in optical characteristics between the present invention and **Lange** is considered to be attributed to the difference in structure. More detailed explanations on this point are given below.

Lange uses non-agglomerated silica particles (i.e., spheres) in preparation of the coating composition. Such non-aggregated spherical particles naturally tend to be closely packed as shown in Fig. 9 of the present application, while it is **extremely difficult** to cause such irregular packing as would form large pores having a size large than the size of independent spherical particle. It is easily imaginable that if large pores are forcibly

formed by some measure, the resultant porous silica coating becomes **fragile** such that the porous silica coating is **no longer** applicable to practical use.

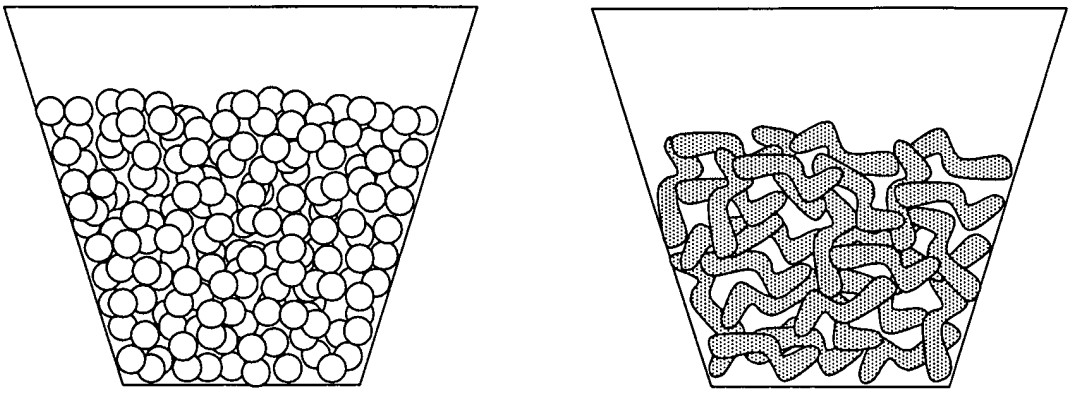
On the other hand, the coated article of the present invention is produced by the use of a coating composition prepared by mixing **moniliform silica strings** (which has been formed **in advance**) with a **hydrolyzable group-containing silane** (which serves as a silane coupling agent) to thereby enable the formation of **large pores** in a silica coating **without sacrificing the strength** of the silica coating. As explained in the applicant's response filed on May 22, 2007, the moniliformed silica strings are formed by a specific method, such as the **specific 4-step process** in Watanabe et al. (US 6632489) which involves **mixing of two different types** of silica particles and **elevation of the pH** from "2 to 6" to "**7 to 10**".

As a simple metaphor for illustratively showing the difference in structure between the porous silica coating according to the present invention and the porous silica coating according to **Lange**, the technique of **Lange** can be likened to the case where a large number of beads (corresponding to the non-agglomerated silica particles) are packed into a container, whereas the technique of the present invention can be likened to the case where the ir-

regularly shaped sticks (corresponding to the monoliform silica strings) coated with an adhesive (corresponding to the hydrolyzable group-containing silane) are packed into a container. This metaphor is illustratively shown in Fig. B below.

Fig. B

Lange Present Invention



3. Conclusion:

From the above, it is apparent that the reflectance of the coated article of **Lange** is **1.0 % at the lowest** (measured at a wavelength of 600 nm with respect to one surface of the sample), which is still **higher than** the reflectance (0.1 to 0.45 %) recited in claim 1 of the present application. Further, the calculated refractive in-

dex (with respect to one surface of the sample) is **1.382 at the lowest**, which is still **higher than** the refractive index (1.22 to 1.30) recited in claim 1 of the present application.

With respect to the relationship between the porosity of the porous silica coating and the refractive index (RI), which is represented by the formula shown at col. 4, line 45 of **Lange**, such a relationship is **nothing more than a generally theory**, and does **not** mean that **Lange** can provide a silica coating having an "index of refraction of from about 1.15 to 1.40, preferably 1.20 to 1.30" **without sacrificing** the strength of the silica coating.

The only optical characteristic that is actually measured in **Lange** is the transmittance from which the above-mentioned reflectance and refractive index are determined.

Therefore, it is apparent that the optical characteristics (the refractive index and the minimum reflectance) as recited in claim 1 of the present application can**not** be achieved by **Lange** while maintaining the strength of the porous silica coating at a practically acceptable level (i.e., a pencil hardness of H or higher as measured in accordance with JIS K5400 under a load of 1 kg, using a testing pencil as defined in JIS S6006).

Exhibit 2

Experiments to evaluate the reflectance of the "coated articles" produced in the Examples of U.S. Patent No. 4,816,333 (**Lange**), and the refractivity and strength of the silica coatings of the coated articles

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1. Object of the experiments:

In Exhibit 1, it is shown that the data shown in the Examples of **Lange** indicates that the reflectance of the coated article of **Lange** is **1.0 % at the lowest** (measured at a wavelength of 600 nm with respect to one surface of the sample), which is still **higher than** the reflectance (0.1 to 0.45 %) recited in claim 1 of the present application.

Further, in Exhibit 1, it is pointed out that the optical characteristics (the refractive index and the minimum reflectance) as recited in claim 1 of the present application can**not** be achieved by **Lange** while maintaining the strength of the porous silica coating at a practically acceptable level (i.e., a pencil hardness of H or higher as measured in accordance with JIS K5400 under a load of 1 kg, using a testing pencil as defined in JIS S6006).

In order to substantiate this, experiments are per-

formed below.

2. Methods and Materials:

Coated articles were produced by substantially the same methods as in Example 1, Example 3 (Comparative Example) and Example 5 of **Lange**, and the optical and physical properties of the obtained coated articles were evaluated. The materials and evaluation methods were as follows.

(2-1) Materials

Colloidal silica: Nalco 2326 (ammonia stabilized colloidal silica; 14.5% colloidal silica as SiO_2; particle size 5 nm; available from Nalco Chemical Company)

PET film: "Cosmoshine A4100"[1] (PET film for optical use, manufactured and sold by Toyobo Co., Ltd., Japan) which has a thickness of 125 μm, and a highly smooth surface and an easy adhesion surface

PMMA film: Transparent polymethylmethacrylate (PMMA) film produced and sold by Asahi

[1] The reason for the choice of this PET film is as follows. Generally, commercially available PET films for optical use are treated on both surfaces thereof. With respect to the surface treatment of the PET film, **Lange** has no description. Since it is expected that the surface treatment may affect the optical characteristics, "Cosmoshine A4100" which has both a treated surface and an untreated surface is used in the present experiments.

Kasei Chemicals Corporation, Japan
(thickness :
0.8 mm)

(2-2) Evaluation methods

• Measurement of reflectance:

A portion of the undersurface of a sample (i.e., a portion of the surface remote from the porous silica layer) was roughened with sandpaper and the roughened surface was coated with black ink, so as to prevent incident light rays from being reflected on the undersurface of the sample. Then, the reflectance at an incidence angle of 12° was measured using a spectrophotometer (trade name: MPC-2200; manufactured and sold by Shimadzu Corporation, Japan).

• Calculation of the refractive index:

The refractive indices of the samples are calculated by an add-in software for Microsoft Excel, which is contained in a CD-ROM attached to a book entitled "Simulation Technique and Optimal Design about Optical Multilayered Films by Excel VBA", published by Technical Information Institute Co., Ltd., Japan.

• Measurement of pencil hardness:

The pencil hardness was measured in accordance with JIS K5400 under a load of 1 kg, using a testing pencil as defined in JIS S6006. More specifically, the coated surface of the sample was scratched 5 times under a load of 1kg using the testing pencil.

Experiment 1 (corresponding to Example 1 of **Lange**)

1 g of Nalco 2326 (colloidal silica) was added to 4.8 g of ethanol, followed by stirring, to thereby obtain a coating composition having an SiO_2 content of 2.5 %. (In this connection, it should be noted that, in Example 1 of **Lange**, the SiO_2 content was 0.83 %; however, a coating having a thickness described in Example 1 of **Lange** could not be obtained using a colloidal silica having an SiO_2 content of 0.83 %. Therefore, in the instant experiment, the SiO_2 content was increased to 2.5 % so as to form a coating having a thickness as described in Example 1 of **Lange**.)

The obtained coating composition was applied onto the highly smooth surface of the PET film ("Cosmoshine A4100") by a bar coater to form a coating (a). The formed coating (a) was air-dried, followed by heating at 100 °C for 2 minutes, to thereof obtain a sample (a) (coated article).

Experiment 2 (corresponding to Example 1 of **Lange**)

Substantially the same procedure as in Experiment 1 was repeated except that the coating composition was applied onto the easy adhesion surface of the PET film, to thereby obtain a sample (b) (coated article) having a coating (b).

Experiment 3 (corresponding to Examples 3 (Comparative) and Example 5 of **Lange**)

The "Solution I" as shown in a Table at col. 7, lines 55 to 62 of **Lange** is produced, and used as a coating composition.

The obtained coating composition was applied onto one surface of the PMMA film by a bar coater, to thereby form a coating (c). The formed coating (c) was air-dried, followed by heating at 80 °C for 3 minutes, to thereof obtain a sample (c) (coated article). The obtained sample was allowed to stand for 1 hour and, then, subjected to the above-mentioned evaluations.

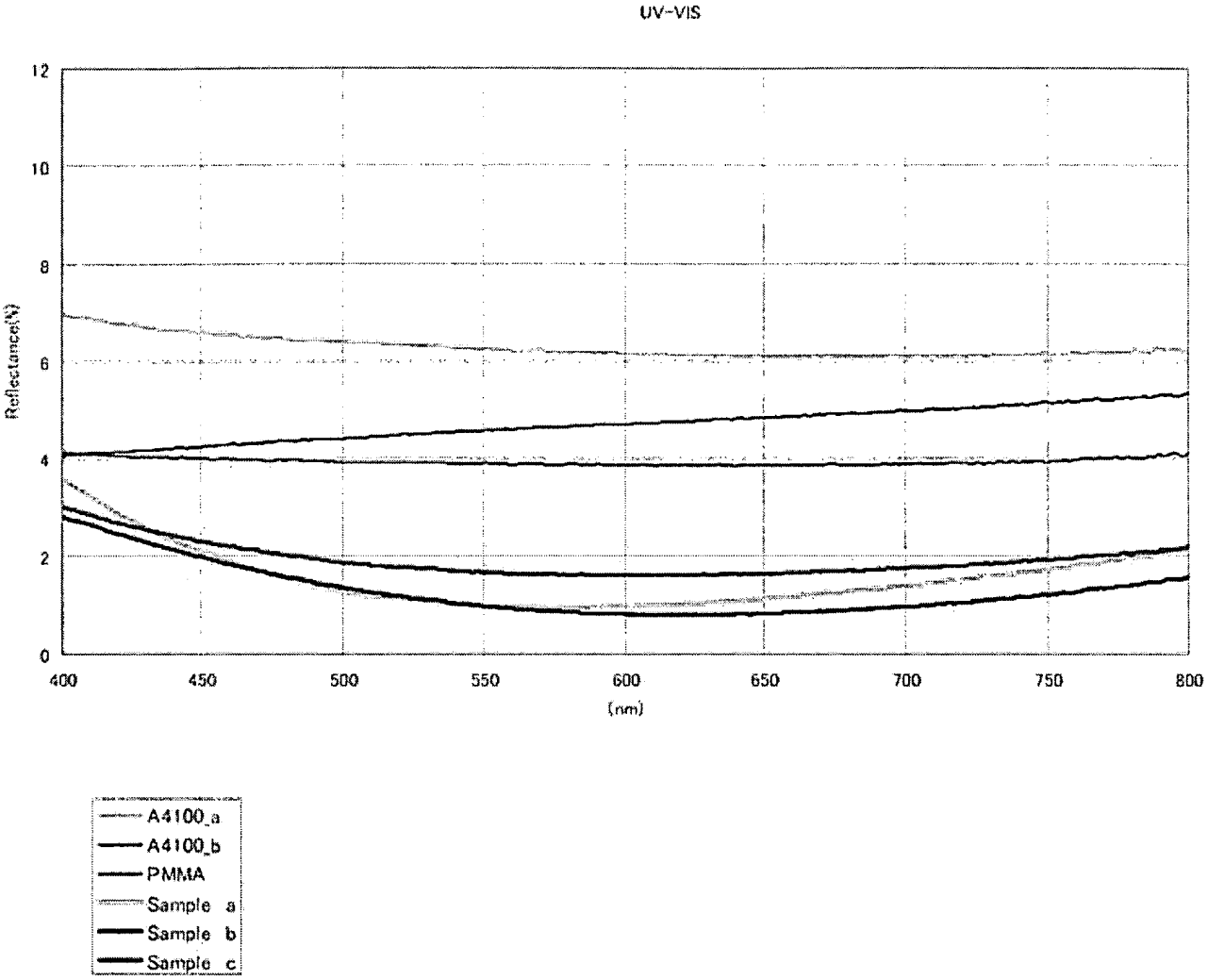
3. Results:

3-1) Reflectance

The results of the evaluation of reflectance of the samples obtained in Experiments 1 to 3 are shown in Fig. 1

below.

Fig. 1



Note:

"A4100a" means the reflectance spectrum of the highly-smooth surface of the PET film "A4100".

"A4100b" means the reflectance spectrum of the easy adhesion surface of the PET film "A4100".

"PMMA" means the reflectance spectrum of the PMMA film (thickness: 0.8 mm).

"Sample a", "Sample b" and "Sample c", respectively, mean the reflectance spectra of the above-mentioned sample (a), sample (b) and sample (c).

Fig. 1 above shows that the reflectance of the coated article produced in accordance of **Lange** (at all wavelengths including those used in the present application for the measurement of minimum reflectance) is **much higher** than the range (0.1 to 0.45 %) recited in claim 1 of the present application.

3-2) Refractive index

From the reflectance values shown in Fig. 1, the reflective indices are calculated by the method mentioned in items (2-2) above. The results are shown in Table 1 below.

Table 1

	Sample	Refractive index	Thickness (nm)
Experiment 1	PET film (A4100) Highly smooth surface	1.660	---
	PET film (A4100) Easy adhesion layer	1.605	100
	Coating (a) of sample (a)	1.421	102
Experiment 2	Coating (b) of sample (b)	1.364	116
Experiment 3	PMMA film	1.490	---
	Coating (c) of sample (c)	1.387	109

Table 1 above shows that the refractive index of the silica coating formed in accordance with **Lange** is 1.364 at the lowest, which is still higher than the range (1.22 or more and less than 1.30) recited in claim 1 of the present application.

3-3) Pencil hardness

With respect to sample (a), the coating (a) was delaminated at the 5th scratch.

With respect to sample (b), the coating (b) suffered narrow scratch lines at the 5th scratch.

With respect to sample (c), the coating (c) suffered narrow scratch lines at the 5th scratch.

Further, with respect to all of samples (a), (b) and (c), when the surface of the samples were rubbed by an eraser to erase the lines drawn by the pencil as prescribed in JIS K5400, the coatings were delaminated.

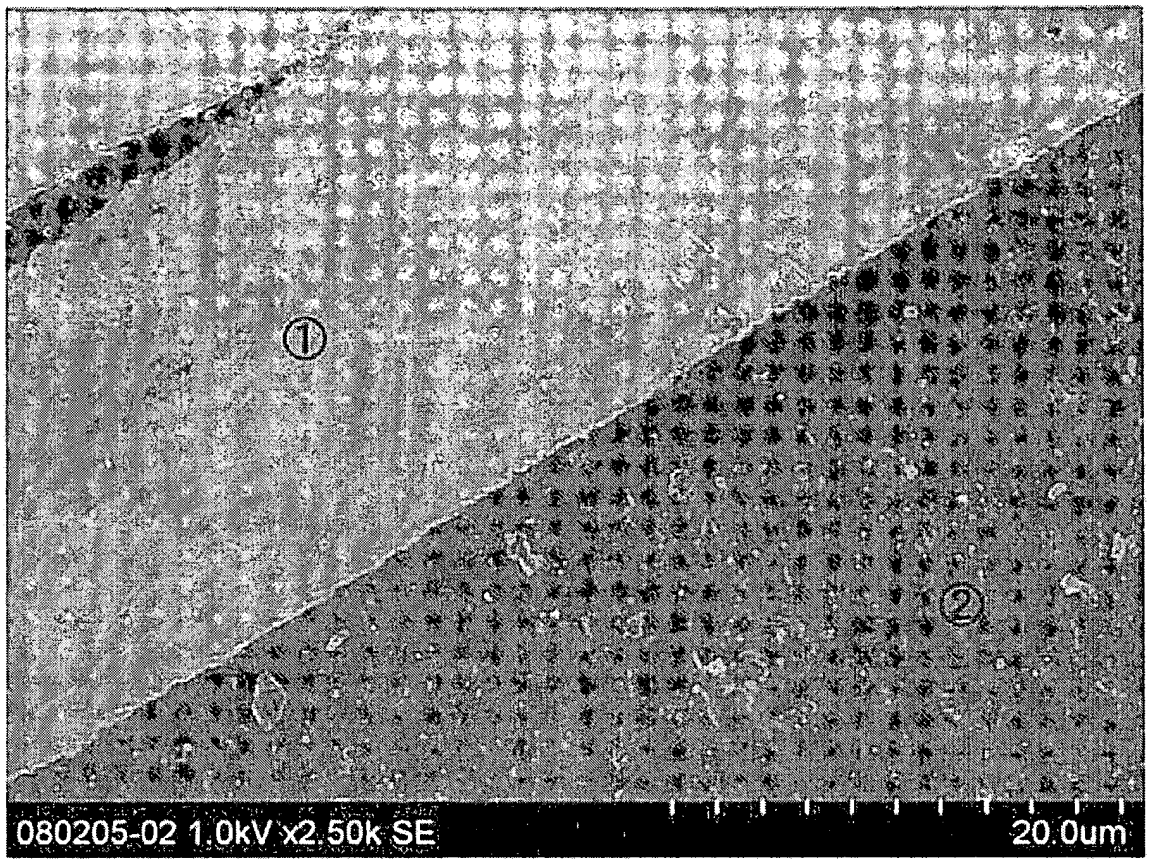
More specific explanations are made below.

3-3-i) Results of scratch by an H pencil (before rubbing with an eraser)

Sample (a):

The surface of coating (a) was observed (at a portion thereof positioned at the boundary between the pencil-scratched area and the non-scratched area) by a scanning electron microscope (SEM) (S-5500, manufactured and sold by Hitachi High-Technologies Corporation, Japan), wherein an osmium plasma coating (thickness : 1 nm) was formed on the surface of the sample prior to the observation, and the magnification was × 2,500. The SEM image is shown in Fig. 2-a-1 below.

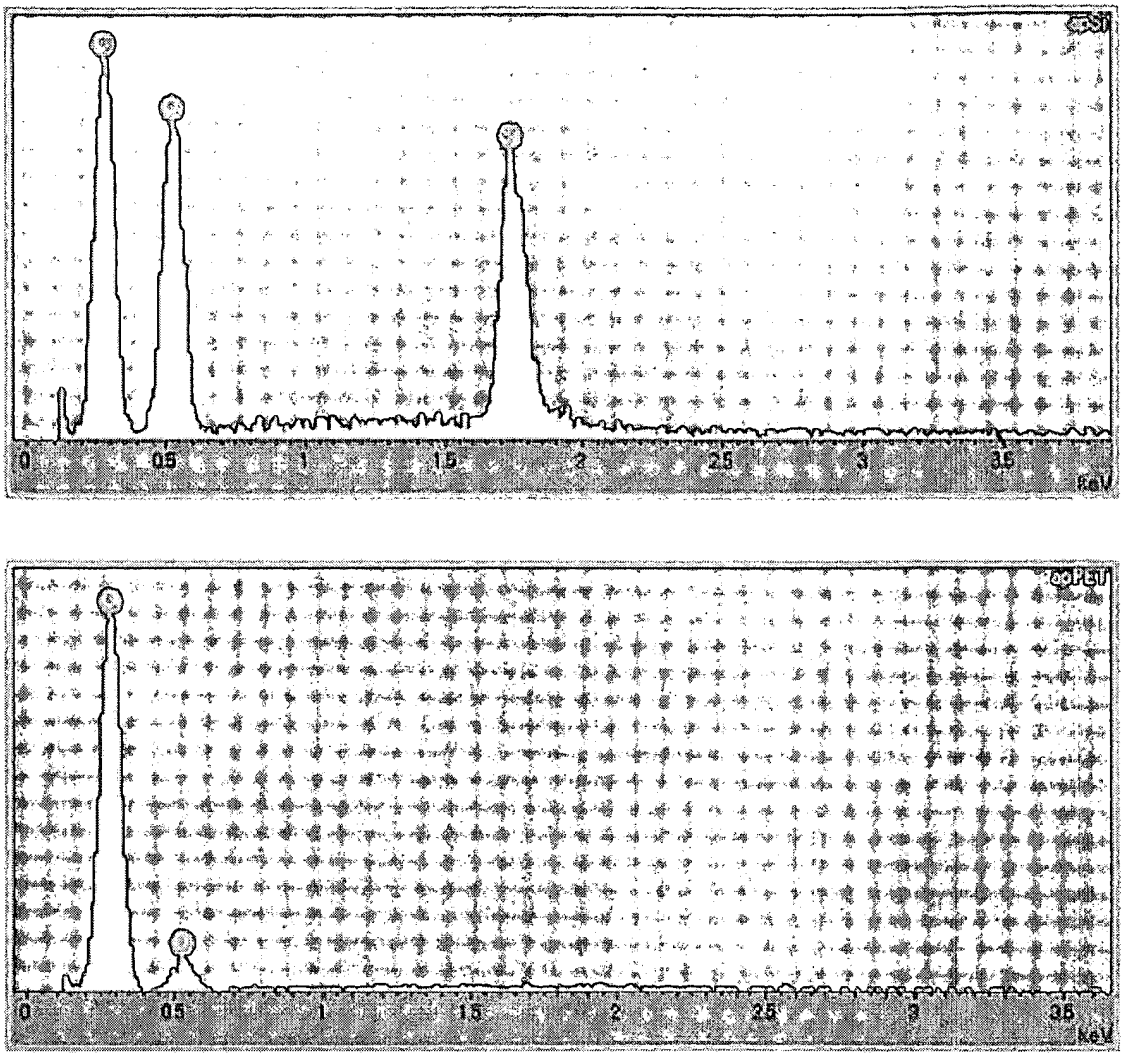
Fig. 2-a-1



In Fig. 2-a-1, the lighter area is the surface of silica coating (a), and the darker area is a portion scratched by the pencil.

With respect to the portions designated ① and ② in Fig. 2-a-1, an elemental analysis was conducted by an energy dispersive X-ray spectrometer (EDX) (E-Max Energy, manufactured and sold by Horiba, Ltd., Japan). The results are shown in Fig. 2-a-2 below.

Fig. 2-a-2



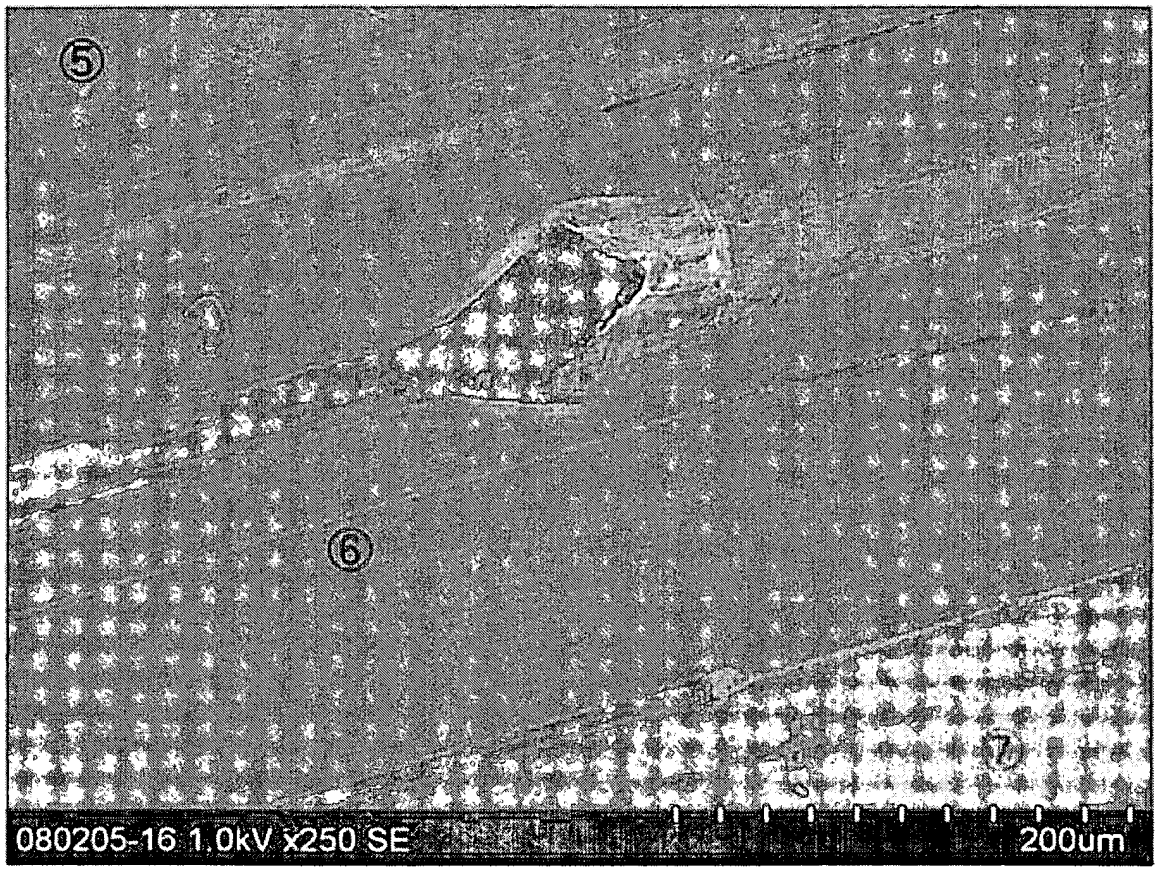
As shown in Fig. 2-a-2, in portion ① (non-scratched portions), a Kα peak around 1.75 KeV which is ascribed to Si is observed, whereas in portion ② (scratched portion), **no** Kα peak is observed around 1.75 KeV.

Thus, it has been confirmed that coating (a) was delaminated by scratch with the H pencil.

Sample (b):

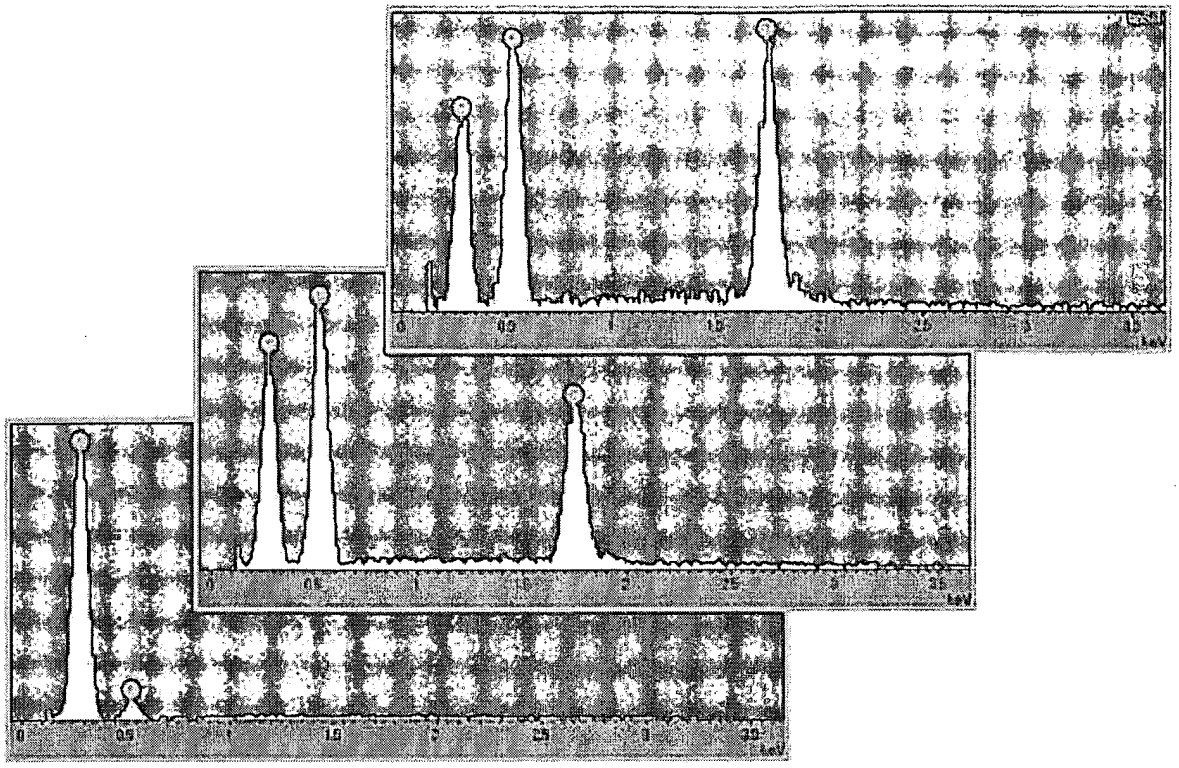
The SEM observation and the EDX analysis were performed in the same manners as in the case of Sample (a). The SEM image is shown in Fig. 2-b-1 below.

Fig. 2-b-1



With respect to the portions designated ⑤, ⑥ and ⑦ in Fig. 2-b-1, an elemental analysis was conducted by EDX, the results of which are shown in Fig. 2-b-2 below.

Fig. 2-b-2



As shown in Fig. 2-b-2, in each of portions ⑤ and ⑥ (non-scratched portions), a Kα peak around 1.75 KeV which is ascribed to Si is observed, whereas in portion ⑦ (scratched portion), **no** Kα peak is observed around 1.75 KeV.

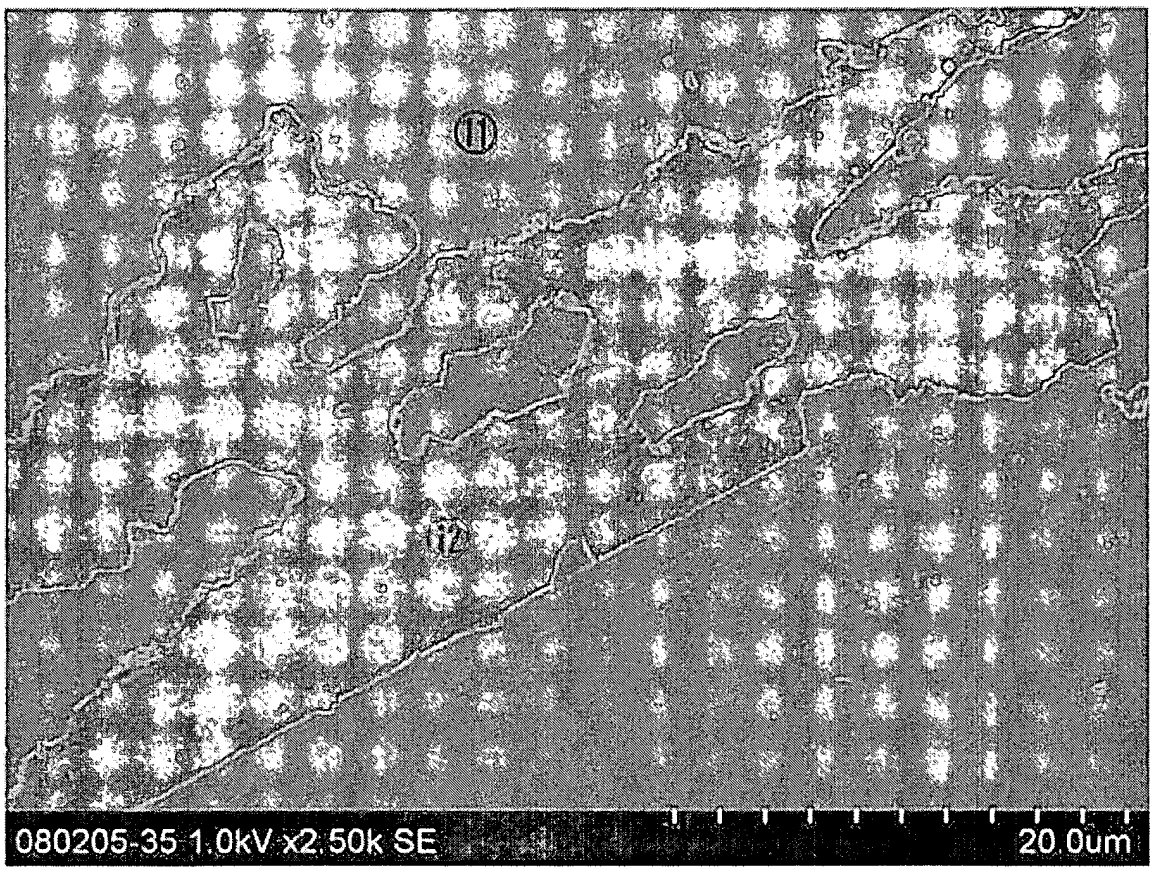
Thus, it has been confirmed that coating (b) was delaminated by scratch with the H pencil.

Sample (c):

The SEM observation and the EDX analysis were per-

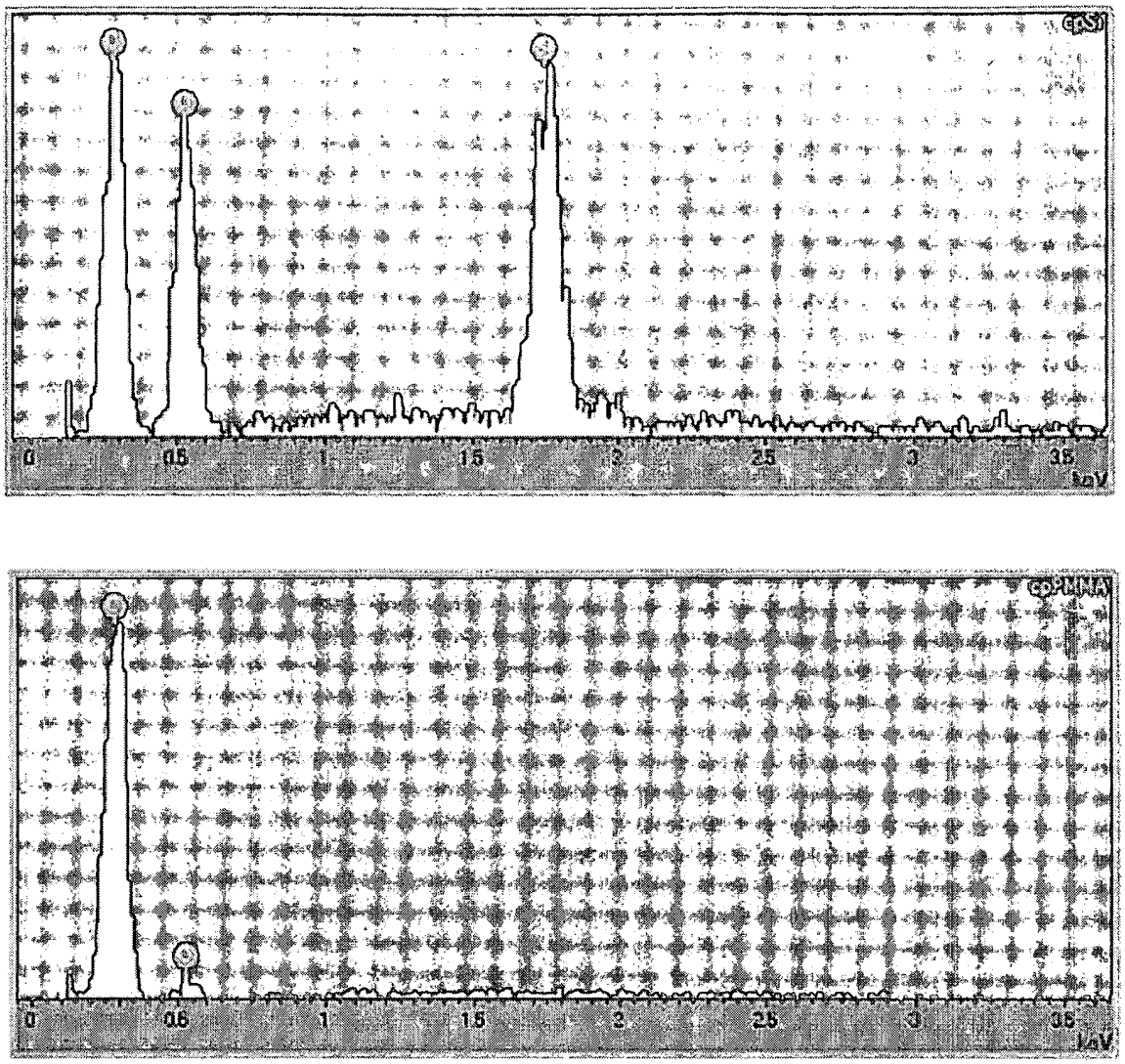
formed in the same manners as in the case of Sample (a). The SEM image is shown in Fig. 2-c-1 below.

Fig. 2-c-1



With respect to the portions designated ⑪ and ⑫ in Fig. 2-c-1, an elemental analysis was conducted by EDX, the results of which are shown in Fig. 2-c-2 below.

Fig. 2-c-2



As shown in Fig. 2-c-2, in portion ⑪ (non-scratched portion), a Kα peak around 1.75 KeV which is ascribed to Si is observed, whereas in portion ⑫ (scratched portion), **no** Kα peak is observed around 1.75 KeV.

Thus, it has been confirmed that coating (c) was delaminated by scratch with the H pencil.

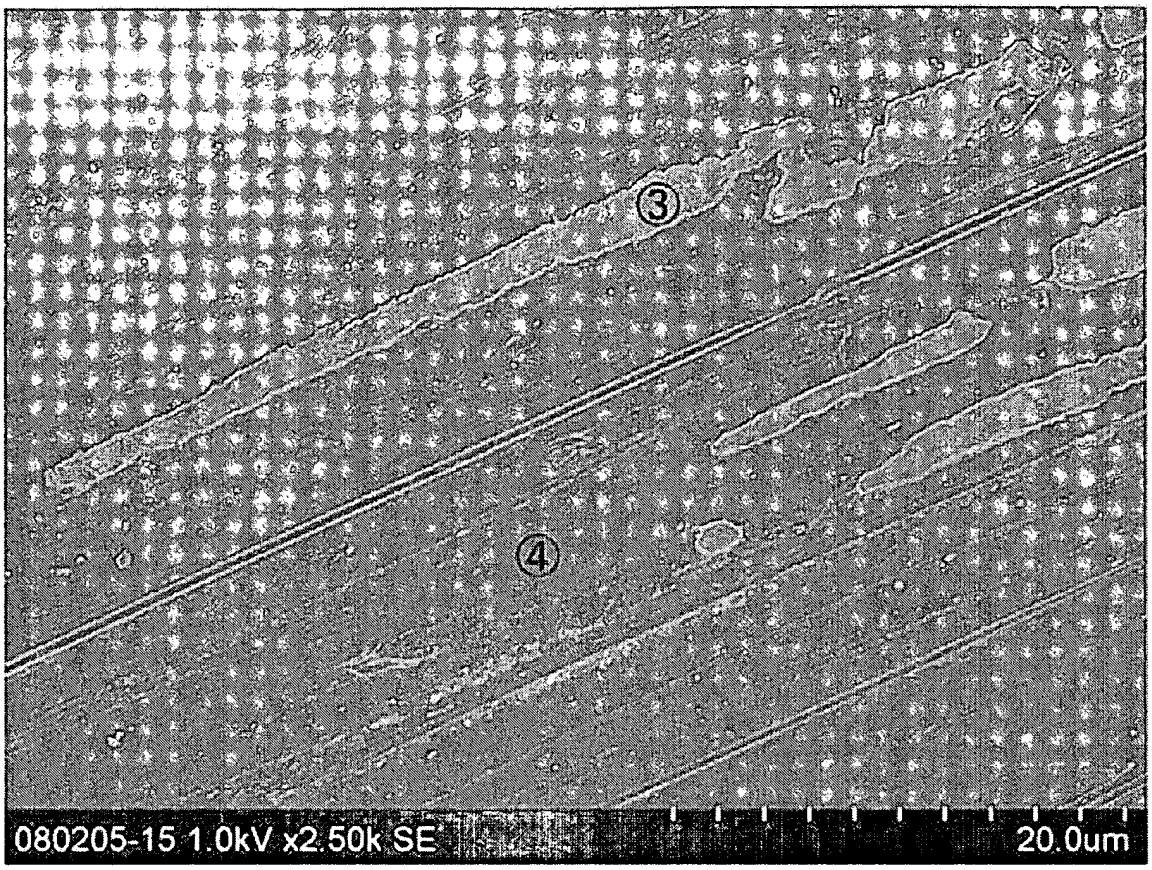
From the above, it is apparent that the pencil hardness of the silica coating formed in accordance with **Lange** is lower than "H".

3-3-ii) Results of rubbing by an eraser

Sample (a):

The surface of coating (a) was observed (at a portion thereof which had been rubbed with an eraser) by SEM in the same manner as mentioned in item 3-3-i) above. The SEM image is shown in Fig. 3-a-1 below.

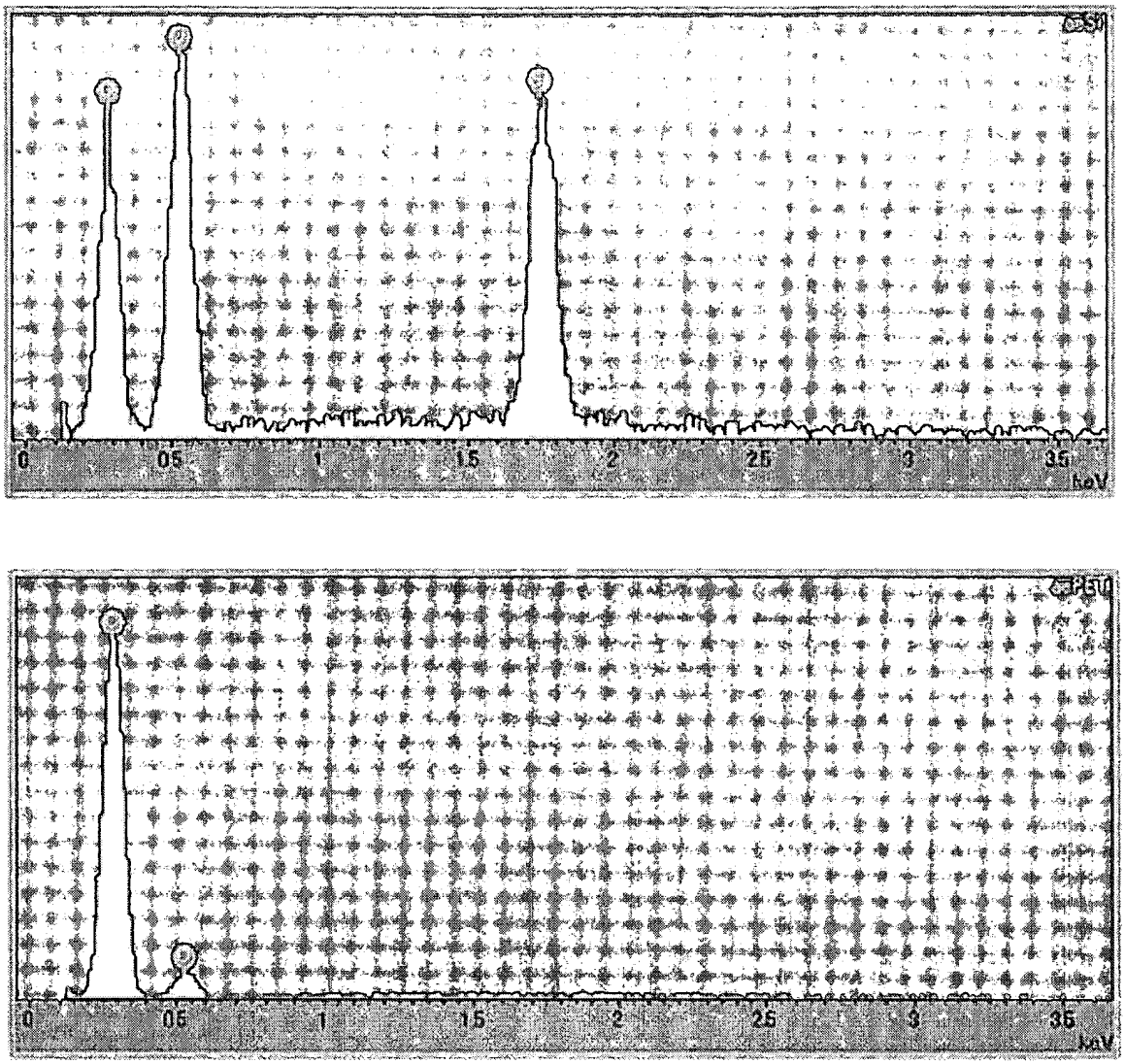
Fig. 3-a-1



In Fig. 3-a-1, the lighter area is silica coating (a) remaining on the surface of sample (a), and the darker area is a portion where silica coating (a) has been de-laminated by the pencil scratch.

With respect to the portions designated ③ and ④ in Fig. 3-a-1, an elemental analysis was conducted by EDX in the same manner as mentioned in item 3-3-i) above. The results are shown in Fig. 3-a-2 below.

Fig. 3-a-2



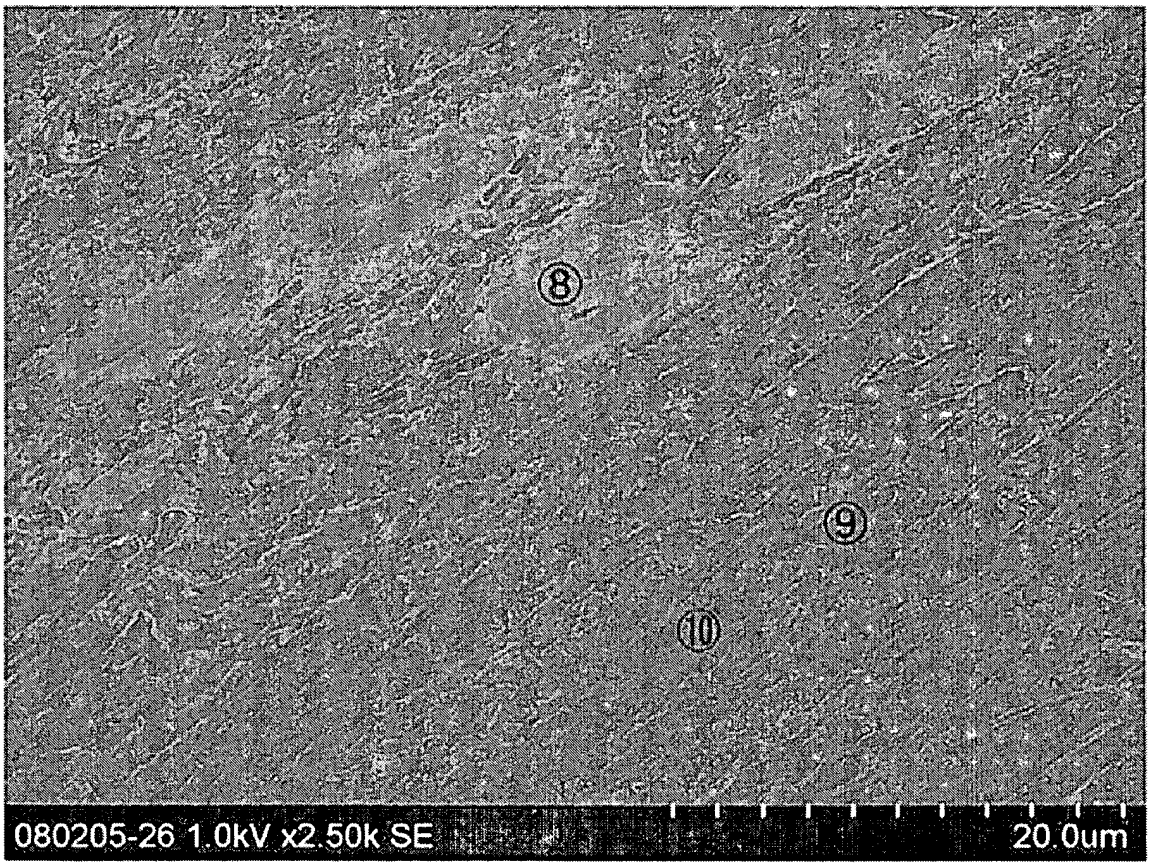
As shown in Fig. 3-a-2, in portion ③ (remaining silica coating), a Kα peak around 1.75 KeV which is ascribed to Si is observed, whereas in portion ④ (delaminated portion), **no** Kα peak is observed around 1.75 KeV.

Thus, it has been confirmed that coating (a) was delaminated by rubbing with an eraser.

Sample (b):

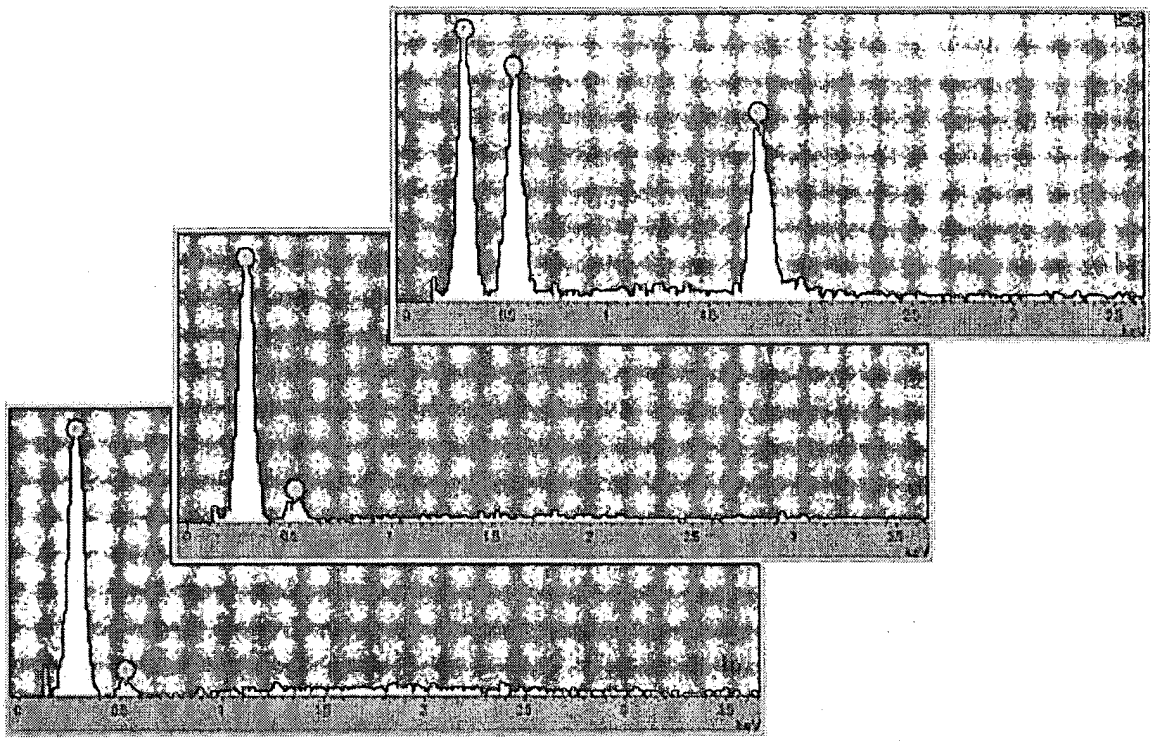
The SEM observation and the EDX analysis were performed in the same manners as in the case of Sample (a). The SEM image is shown in Fig. 3-b-1 below.

Fig. 3-b-1



With respect to the portions designated ⑧, ⑨ and ⑩ in Fig. 3-b-1, an elemental analysis was conducted by EDX, the results of which are shown in Fig. 3-b-2 below.

Fig. 3-b-2



As shown in Fig. 3-b-2, in portion ⑧ (remaining silica coating), a Kα peak around 1.75 KeV which is ascribed to Si is observed, whereas in each of portions ⑨ and ⑩ (delaminated portions), **no** Kα peak is observed around 1.75 KeV.

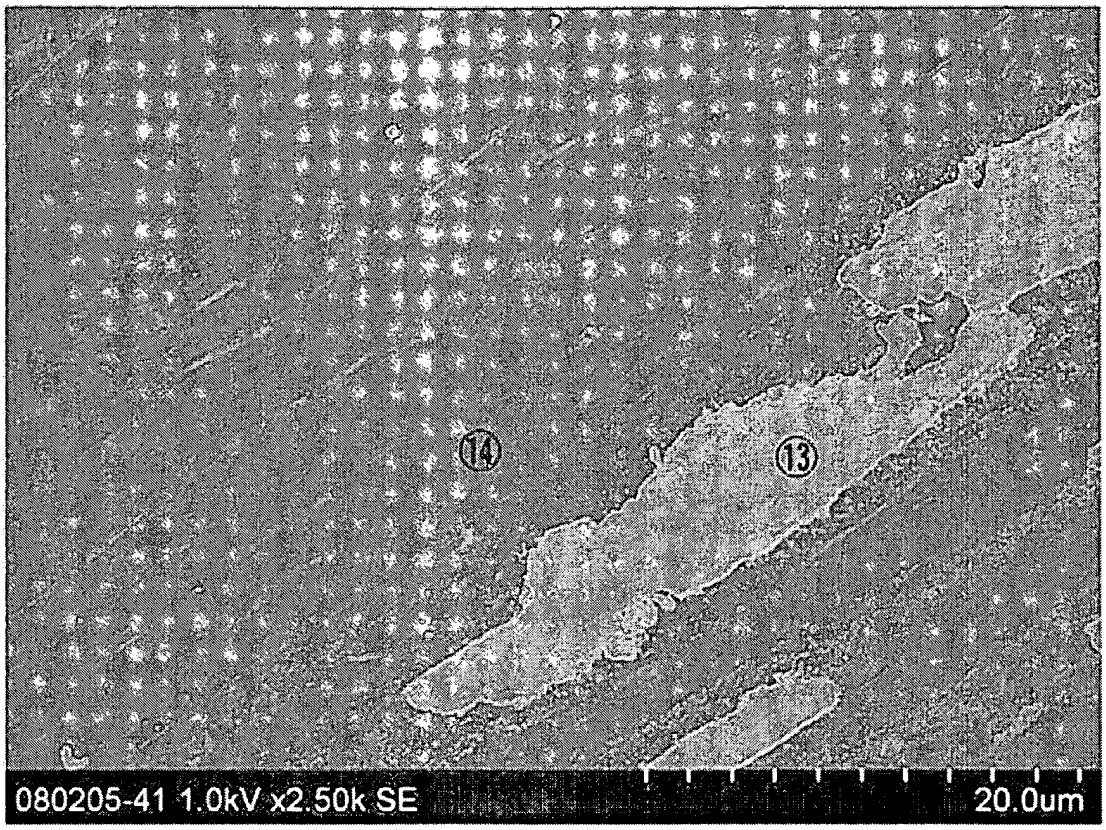
Thus, it has been confirmed that coating (b) was delaminated by rubbing with an eraser.

Sample (c):

The SEM observation and the EDX analysis were per-

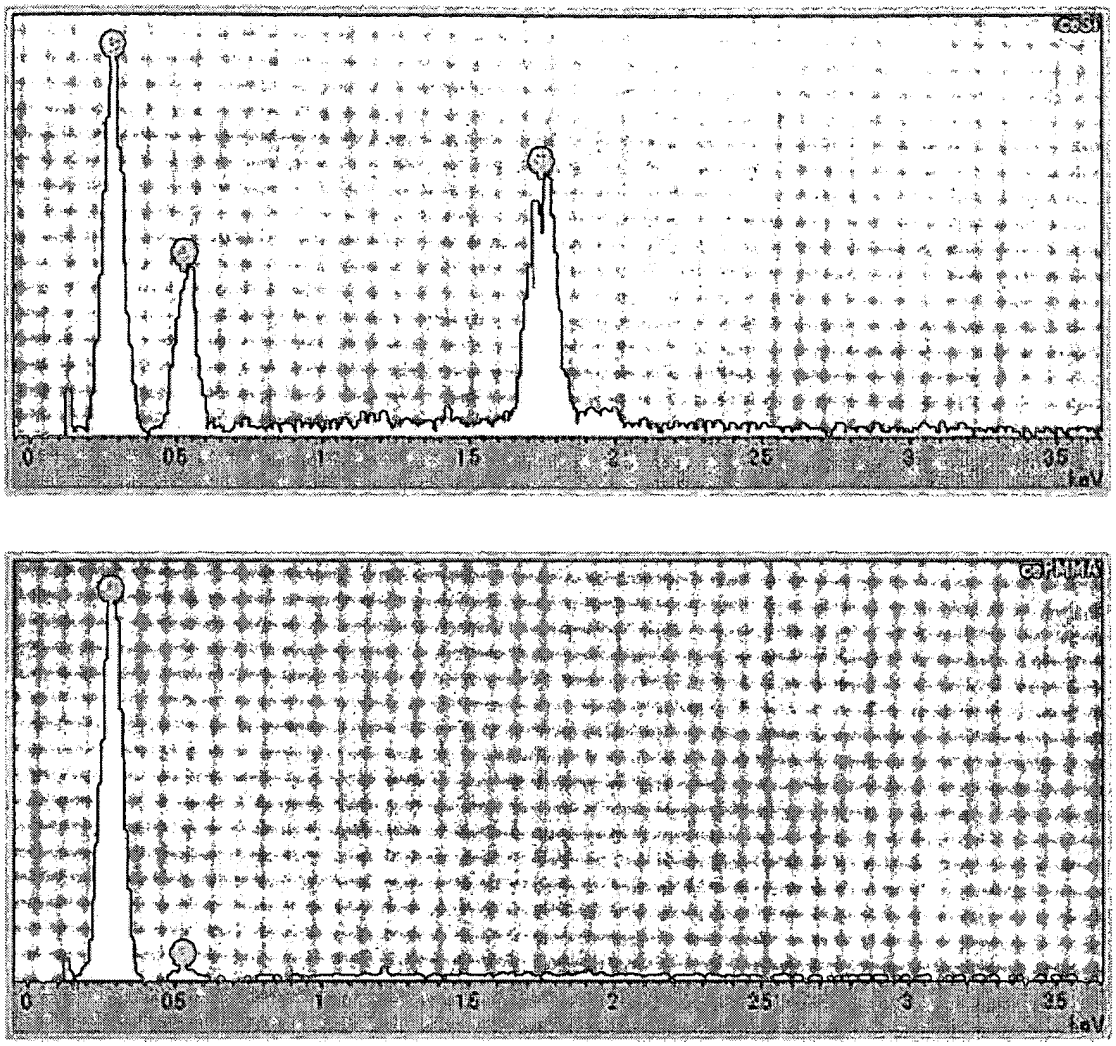
formed in the same manners as in the case of Sample (a). The SEM image is shown in Fig. 3-c-1 below.

Fig. 3-c-1



With respect to the portions designated ⑬ and ⑭ in Fig. 3-c-1, an elemental analysis was conducted by EDX, the results of which are shown in Fig. 3-c-2 below.

Fig. 3-c-2



As shown in Fig. 3-c-2, in each of portion ⑬ (remaining silica coating), a Kα peak around 1.75 KeV which is ascribed to Si is observed, whereas in portion ⑭ (delaminated portions), **no** Kα peak is observed around 1.75 KeV.

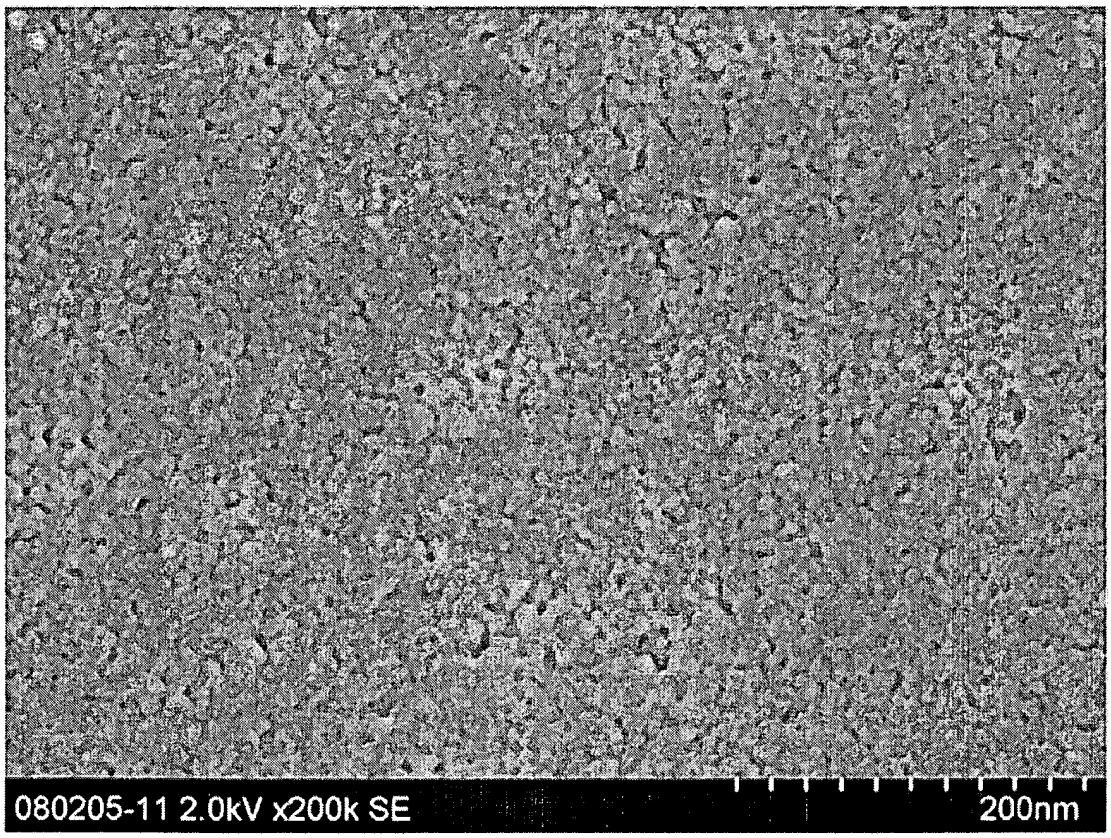
Thus, it has been confirmed that coating (c) was delaminated by rubbing with an eraser.

3-3-iii) Observations of the nano-structures of the silica coatings

Sample (a):

The surface of coating (a) was observed by SEM in the same manner as in item 3-3-ii) above, except that the magnification was increased from × 2,500 to × 200,000. The image obtained by the SEM observation is shown in Fig. 4-a below.

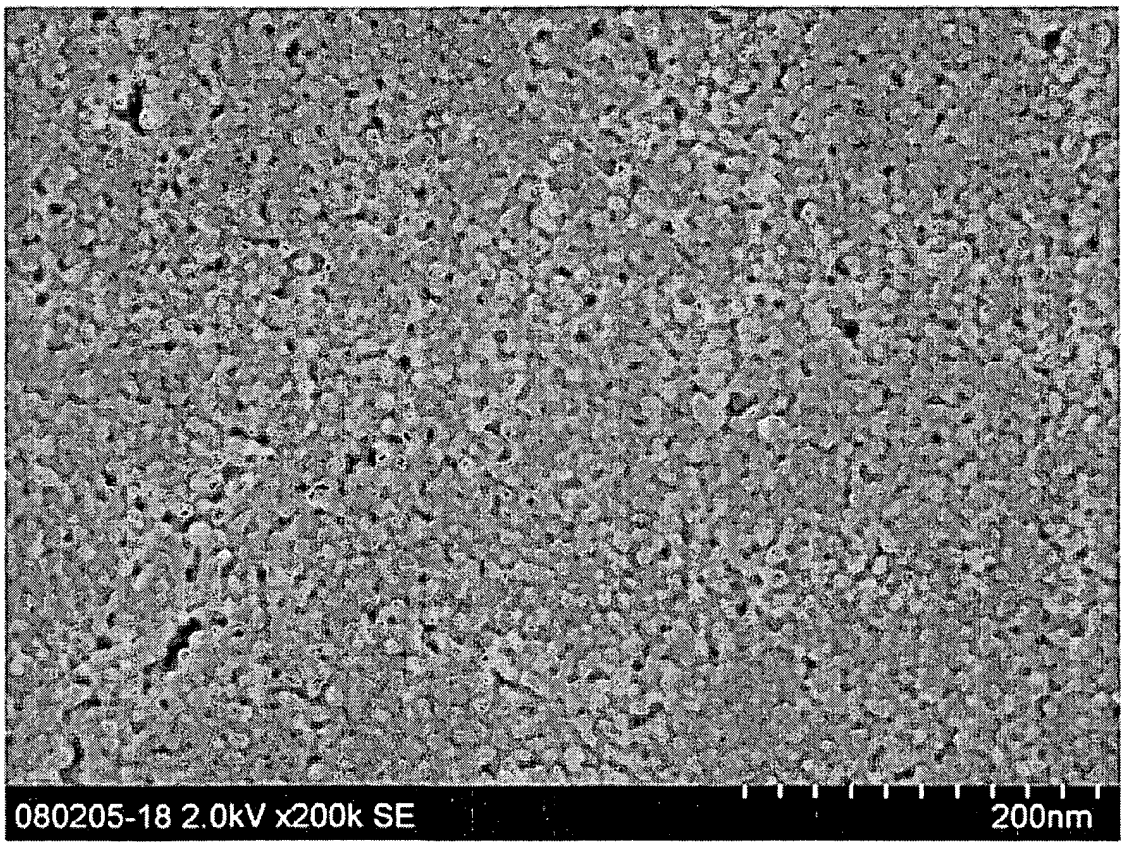
Fig. 4-a



Sample (b):

The SEM observation (× 200,000) of the surface of sample (b) was conducted in the same manner as in the case of sample (a). The SEM image obtained by the observation is shown in Fig. 4-b below.

Fig. 4-b

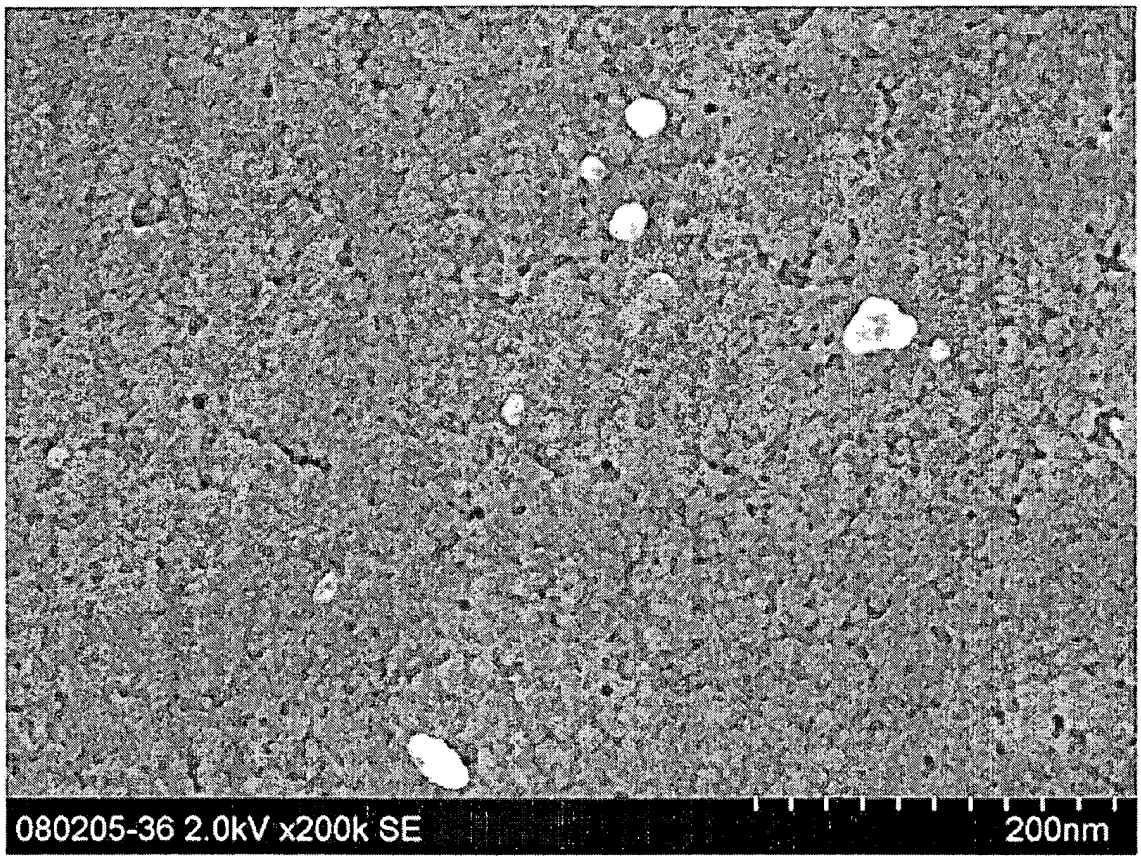


Sample (c):

The SEM observation (× 200,000) of the surface of sample (c) was conducted in the same manner as in the case

of sample (a). The SEM image obtained by the observation is shown in Fig. 4-c below.

Fig. 4-c



From Figs. 4-a, 4-b and 4-c, it can be seen that, in the silica coatings formed by the technique of **Lange**, most of the silica particles are closely packed, while some irregularity is observed in the arrangement of the silica particles.

In this connection, it should be noted that the nano-structures of the silica coatings as shown in Figs. 4-a, 4-b and 4-c are similar to that shown in Fig. 9 of the present application.

4. Conclusion:

As can be seen from Fig. 1, the reflectance of the coated article produced in accordance of **Lange** (at all wavelengths including those used in the present application for the measurement of minimum reflectance) is much higher than the range (0.1 to 0.45 %) recited in claim 1 of the present application.

Further, as can be seen from Table 1, the refractive index of the silica coating formed in accordance with **Lange** is 1.364 at the lowest, which is still higher than the range (1.22 or more and less than 1.30) recited in claim 1 of the present application.

Further, as can be seen from Figs. 2-a-1, 2-a-2, 2-b-1, 2-b-2, 2-c-1, 2-c-2, 3-a-1, 3-a-2, 3-b-1, 3-b-2, 3-c-1 and 3-c-2, the silica coating formed in accordance with **Lange** has a pencil hardness lower than "H".

From Figs. 4-a, 4-b and 4-c, the above-mentioned poor optical characteristics and poor strength in **Lange** (as compared to the present invention) are attributable to the

difference in structure of the silica coatings.

Thus, it has been confirmed that, by the technique of **Lange**, it is impossible to obtain the silica-containing laminated structure of the present invention which is advantageous in that the porous silica layer has not only low refractivity but also high strength.